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Algal-Available Phosphorus in Suspended Sediments from Lower Great Lakes Tributaries

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ALGAL-AVAILABLE PHOSPHORUS IN SUSPENDED SEDIMENTS FROM LOWER GREAT LAKES TRIBUTARIES

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ABSTRACT. *Suspended sediments collected from five tributaries to the lower Great Lakes were chemically analyzed for several forms of phosphorus and bioassayed under aerobic conditions to measure the release of algal-available phosphorus. The bioassay data for all samples, interpreted through a first-order model of available phosphorus release, showed an average of 21.8 percent of the total particulate phosphorus ultimately was available to* Selenastrum capricornutum, *and available phosphorus was released at an average rate of 0.154 day^{-1}. Amounts of available phosphorus varied considerably between tributaries with the Ohio tributaries (Maumee, Sandusky, and Cuyahoga Rivers) showing generally greater amounts than those in New York (Cattaraugus and Genesee Rivers). Non-apatite fractions of inorganic phosphorus (base-, and reductant-extractable) correlated well with levels of available phosphorus in the suspended sediment samples; however, the first-order release coefficients showed little dependency on the particulate phosphorus characteristics. The results indicate that prediction of phosphorus dynamics in the lower Great Lakes may be made with greater accuracy than current models allow by considering available phosphorus to be released from an ultimately-available fraction of the total particulate phosphorus during residence in the water column.*

INTRODUCTION

The utility of phosphorus load regulation as the primary means of controlling eutrophication in the Great Lakes has been widely accepted (Task Group III 1978). As might be anticipated from the nature of the problem, the lakes most affected culturally, Lakes Erie and Ontario, are those which will require the greatest reductions in phosphorus load and, consequently, the greatest expenditures of effort and resources in order to reverse the trend toward eutrophy. Although point source controls, such as chemical precipitation during municipal wastewater treatment, have become extremely important and necessary components of plans to regulate phosphorus loads to the Great Lakes (IJC 1970, 1972, 1978), the magnitude of diffuse sources of phosphorus to the lower lakes has been such (PLUARG 1978) that non-point source controls also will be required to meet the target load objectives recommended for these lakes (Task Group III 1978, Gregor and Johnson 1980).

A factor which complicates interpretation and application of phosphorus loading data to the lower Great Lakes is the unknown biological availability of the phosphorus loads (PMSTF 1980). Different sources provide the lakes with a variety of forms of phosphorus, in variable proportions, and not all forms are utilized to the same degree or at the same rate. The question of availability, however, acquires a special significance in relation to eutrophication control since identification of those sources which provide relatively high amounts of available phosphorus can permit load control measures to be instituted in a more economical fashion than otherwise would be possible.

An extremely important factor in assessment of the biological effects of phosphorus from any source is the rate at which the phosphorus becomes available to aquatic biota within the receiving water. This is true, as the rate of conversion of potentially-available to actually-available phosphorus competes in time with the rate of other processes, for example: adsorption, precipitation, sedimentation, and dilution. As noted by Verhoff

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and Heffner (1979), however, knowing the amount of ultimately available phosphorus is necessary when the bioavailable conversion rate is rapid relative to the other processes.

Several investigators recently have attempted to relate amounts of available phosphorus, estimated from cell counts and constant cellular phosphorus stoichiometry, to the phosphorus in a variety of chemically defined forms (Williams, Shear, and Thomas 1980; Cowen and Lee 1976; Sagher 1976). The results of these studies indicate that base-extractable forms of particulate inorganic phosphorus and soluble orthophosphate correlate with the growth of algae during short-term incubations (2–4 weeks). Bioavailable phosphorus conversion rates, however, generally have not been measured during availability studies, although estimates have been published (Verhoff and Heffner 1979).

The present investigation was designed to determined experimentally the rate and ultimate extent of biological availability of the phosphorus associated with the suspended solids from major tributaries to the lower Great Lakes. Additionally, a series of chemically-defined fractions of the particulate tributary phosphorus was measured to compare against the bioavailability data in order to examine the relationship between bioavailability and chemical forms of particulate phosphorus in the tributaries. These data provide much-needed information on the rate and extent of availability of particulate tributary phosphorus in the lower Great Lakes region, on the temporal and geographical variability of these quantities within the region, and on the predictability of bioavailable phosphorus characteristics based on relatively rapid chemical analyses.

EXPERIMENTAL AND ANALYTICAL METHODS

Sampling Program

Because tributary monitoring of Lake Erie has shown that more than three-quarters of total phosphorus from diffuse sources is sediment-bound and that most of this nonpoint source is delivered during major late winter-spring runoff events (U.S. Army Corps of Engineers 1979), it was determined that the most representative sampling program for bioavailable sediment phosphorus should be conducted during the runoff season. Furthermore, since the most immediate need is to determine the availability of sediment phosphorus as it enters the lake, all samples from a given tributary were collected at the station closest to its mouth.

Previous studies have indicated three major factors in determining a stream's total and available phosphorus loads: basin geochemistry (Logan 1978); land use activities (Omernik 1976); and agricultural practices (Logan 1977). In order to provide some variability in these factors among the rivers sampled and yet maintain a manageable program, five lower Great Lake tributaries located from western Lake Erie to central Lake Ontario were selected. The five tributary systems are from west to east: Maumee, Sandusky, Cuyahoga, Cattaraugus (South Branch), and Genesee.

A total of 25 samples were collected from the five rivers during event-oriented high flow periods. All samples were grab samples collected at mid-depth of the station. Samples were collected as close as possible to the peak flow of a given runoff event. A listing of the samples collected and date of collection is presented in Table 1. Note that all samples were taken between early March and mid-June.

Sample Handing and Preparation

Approximately 10 liters of each sample were transferred on-site to polyethylene cubitainers. The cubitainers were cooled to 4°C within several hours of collection, packed with frozen ice-packs in large insulated transportation coolers, and shipped to Potsdam via the quickest carrier. Virtually all samples arrived in Potsdam within 24 hours after collection. Upon receipt at Clarkson College, the cubitainers, the contents of which never exceeded 10°C, were stored at 4°C until preparation and analysis.

A two-liter aliquot of each sample was preserved for physical and chemical characterization of the river water at the time of collection. The remainder of the sample, approximately 8 liters, was filtered under positive pressure through a 0.4-μm pore diameter membrane. The non-filterable residue was resuspended in a phosphorus-free, synthetic algal growth medium (Guillard and Lorenzen 1972) to give a suspended solids concentration of about 10 gm/L. This suspended sediment concentrate was stored at 4°C and used for chemical particulate phosphorus fractionation and for bioassay of algal-available particulate phosphorus. Studies showed that sediments stored at 4°C as a concentrate in the algal medium did not release significant amounts of phosphorus.

TABLE 1. List of samples analyzed with flow and suspended solids data at time of collection.

Sample No.	River	Collection Date	Flow* (m^3/s)	Suspended Solids Total (mg/L)	Suspended Solids % < 20 μm*
1	Cuyahoga	3/8/80	142.	590	70.8
2	Sandusky	3/9/80	566.	1028	96.1
3	Genesee	3/20/80	—	156	88.5
4	Cuyahoga	3/22/80	133.	278	66.9
5	Maumee	3/20/80	803.	390	97.8
6	Cattaraugus	3/21/80	64.3	4325	48.2
7	Sandusky	3/22/80	362.	690	96.1
8	Maumee	3/25/80	872.	421	96.6
9	Cattaraugus	3/31/80	32.6	647	64.8
10	Cattaraugus	4/14/80	8.10	150	75.3
11	Sandusky	4/15/80	245.	557	96.2
12	Cuyahoga	4/15/80	130.	195	58.5
13	Maumee	4/15/80	691.	278	93.9
14	Maumee	5/28/80	118.	55	—
15	Sandusky	5/27/80	59.1	535	94.8
16	Maumee	5/20/80	348.	111	—
17	Maumee	6/3/80	898.	453	83.7
18	Sandusky	6/5/80	257.	1020	95.0
19	Maumee	6/10/80	339.	348	98.6
20	Cattaraugus	6/20/80	12.4	—	—
21	Cattaraugus	6/20/80	30.0	—	—
22	Sandusky	6/9/80	60.1	432	—

+Instantaneous flows at time of sample collection, except for Cuyahoga flows which are average daily flow.
*Obtained by passing sample through 20 μm nylon mesh prior to suspended solids analysis.

Physical and Chemical Characterization

Measurements made on the two-liter aliquots pertinent to this report included: suspended solids concentration (total and that fraction which passed a 20-μm nylon mesh), total phosphorus, total filterable phosphorus, and filterable reactive phosphorus. Total suspended solids were measured gravimetrically after drying for one hour at 103°C the non-filterable residue of aliquots of each sample collected on tared 0.4-μm membrane filters (APHA 1975). The modified single-reagent ascorbic acid method of Murphy and Riley (1962) was used to analyze all samples or fractions for reactive phosphorus after preliminary digestion if necessary to convert all phosphorus to the orthophosphate form. The digestion step used in this study was the persulfate digestion procedure (APHA 1975).

The chemical extractions used in this study for the fractionation of particulate tributary phosphorus are shown in Figure 1 and are similar to those used by Logan (1978). The basic fractionation procedure involved sequential extraction of 0.1 gm of tributary suspended sediments in 50-mL volumes of increasingly rigorous extractants, followed by centrifugation for solids separation and phosphorus analysis of each extractant supernatant. Each sample was fractionated in duplicate. The 0.1 gm of tributary sediments used in this analysis were obtained from the sediment concentrate by using the volume required according to a prior determination fo the solids content of the concentrate. Details of the extraction procedures and elimination of interferences in the extractant supernatants can be found in Logan, Oloya, and Yaksich (1979a). The fractionation procedure is based on one of the schemes developed by Williams *et al.* (1971).

Bioassay Procedure

While it is generally accepted that only a bioassay can be used to measure truly available phosphorus, the details of the experimental procedures can vary widely. Examples of the various methods employed can be found in Golterman, Bakels, and Jacobs-

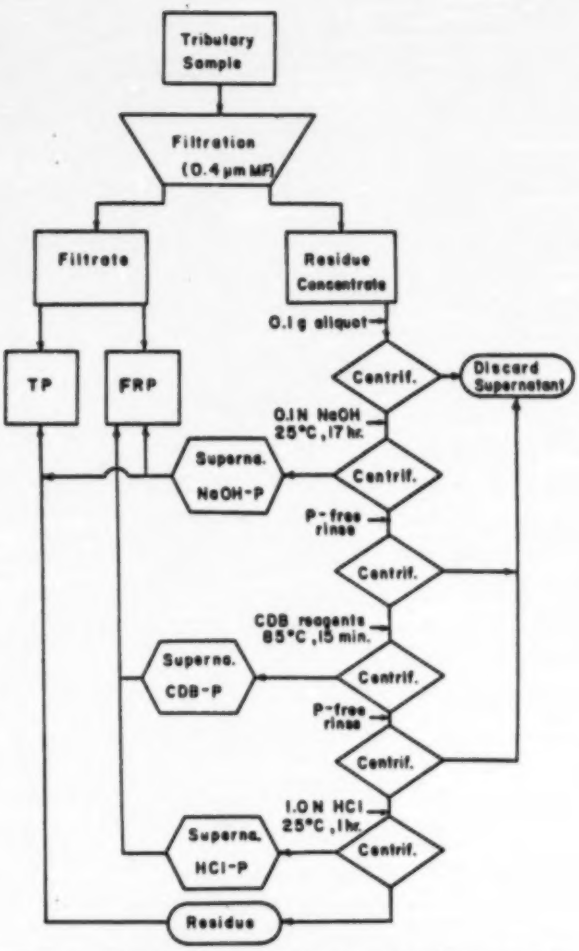

FIG. 1. Chemical characterization of tributary phosphorus (TP = Total P analysis, FRP = Filtrable Reactive P analysis, CDB = Citrate-Dithionite-Bicarbonate reagents, MF = membrane filter).

Mögelin (1969); Cowen and Lee (1976); Sagher (1976); Verhoff and Heffner (1979); and DePinto *et al.* (1980). Logan, Verhoff, and DePinto (1979b) and Lee, Jones, and Rast (1980) have critically reviewed the subject with some discussion of the procedures employed. Because of the need for rate measurements and because of the likelihood of variable phosphorus stoichiometry in the test algal species, we felt that a direct measurement of phosphorus taken up by the test species provided the best approach. Merely relating algal counts to a standard curve is fraught with potential errors, particularly when kinetics are of interest. Furthermore, unless the assay algae are separated from the sediment material, direct measurements of algal phosphorus is very difficult.

Given the above considerations, it was determined that a dual culture approach, similar to that developed in our laboratory (DePinto 1981), would circumvent many of the problems associated with bioassay determination of sediment available phosphorus. The apparatus employed (hereafter referred to as a Dual Culture Diffusion Apparatus - DCDA) allowed the placement of river sediments suspended in lake water in one culture vessel (regeneration vessel) and the placement of a unialgal assay culture with a known phosphorus content in a separate assay vessel (Figure 2). The two vessels were clamped together, but the contents were separated by a 0.4-µm polycarbonate membrane filter. This arrangement permitted repeated, routine sampling of the algae in the assay vessel without disturbing the sediment-water system in the regeneration vessel. The membrane between the two vessels prevented cross-contamination of particulates but allowed cross-diffusion of soluble material including phosphorus released from suspended sediments. Any available phosphorus released by the sediment material in the regeneration vessel, therefore, had a tendency to diffuse across the membrane to the assay vessel where it was rapidly immobilized by the phosphorus-starved algae. A periodic sampling of the phosphorus content of the assay vessel, combined with a mass balance on the system, permitted determination of the rate at which available phosphorus was being released by the sediment.

Depicted in Figure 3 is the bioassay procedure for measurement of the rate and extent to which phosphorus from tributary-suspended sediments becomes available for algal uptake. A typical bioassay experiment was conducted by suspending 100 mg (dry weight) of tributary solids, obtained from an aliquot of the sediment concentrate, in nutrient-spiked (minus phosphorus), filtered Lake Erie water and placing this suspension in the regeneration side of the DCDA. The regeneration vessel was darkened to prevent indigenous algal growth during incubation. All the Lake Erie water used in these experiments was obtained in January, 1980 from the raw water intake at the Buffalo water filtration plant. This water supply was filter-sterilized by pressure filtration through 0.2-µm membrane filters and stored at 4°C until needed. Prior to use in the DCDA, the filtered Lake Erie water was spiked with 1,800 µg NO_3-N/L and the full complement of trace elements recommended by

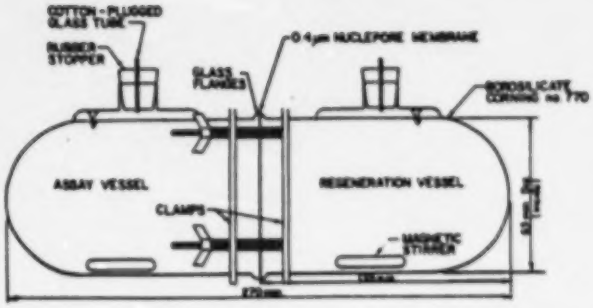

FIG. 2. Schematic of dual culture diffusion apparatus.

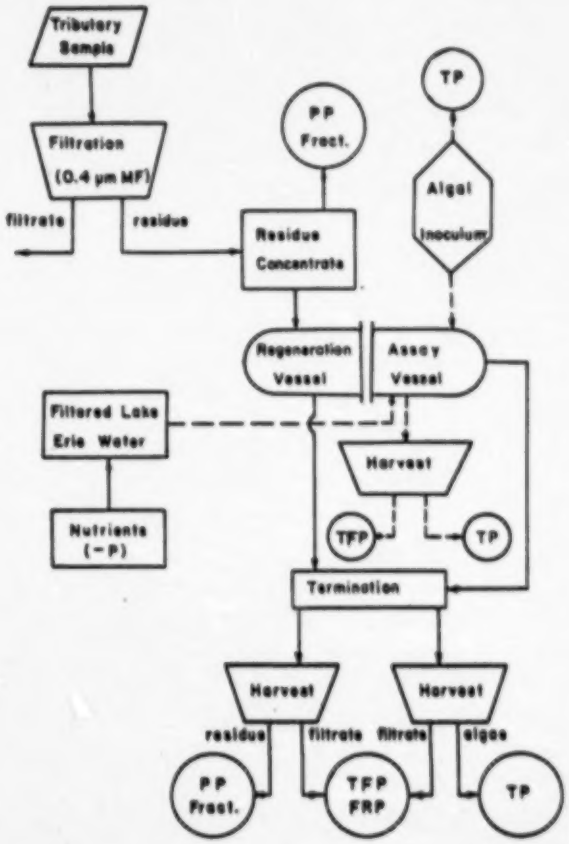

FIG. 3. Flow chart for DCDA evaluation of available particulate phosphorus in tributary samples. Dashed lines are repetitive steps (TP = total phosphorus, PP = particulate phosphorus, TFP = total filtrable P, FRP = filtrable reactive P).

Guillard and Lorenzen (1972) in their freshwater algal medium, thus ensuring phosphorus limitation in the DCDA assay cultures.

The lighted assay vessel of the DCDA contained a 7-day-old culture of phosphorus-starved *Selenastrum capricornutum* which had grown in the filtered and nutrient-spiked Lake Erie water to a known phosphorus content. These assay cultures typically contained 25–30 μg/L total phosphorus, of which virtually all was in the algae. The algae typically had a dry weight biomass of about 30 mg/L (less than 0.1 percent phosphorus by weight).

Following the DCDA start-up described above, both sides of the system were incubated, with magnetic stirring at 25°C, for a period of 4–7 days, depending upon stage of the experiment. After each incubation period, the contents of the assay vessel were completely harvested and analyzed for algal phosphorus. A fresh, 7-day-old *Selenastrum* culture (with known phosphorus content) was then placed into the assay side for a new incubation period. The increase in algal phosphorus in the assay vessel during each incubation period represented the amount of phosphorus that had been released by the sediments, diffused across the membrane and immobilized by the assay algae. The DCDAs were designed so that the bulk diffusion rate across the membrane (2.06 $days^{-1}$) was large enough relative to typical phosphorus release rates (0.1–0.2 $days^{-1}$) so that it was not a rate-limiting process (DePinto 1981).

After a suitable number of incubation periods (long enough for a 3- to 4-week experiment), the experiment was terminated by harvesting both sides of the DCDA and analyzing each for total particulate and total soluble phosphorus. The cumulative release of phosphorus by the sediments and uptake by the algae was used to evaluate the kinetics of the process of available phosphorus release. The above experiment was conducted in triplicate (except where insufficient sediments were available) on all samples in Table 1.

RESULTS

Phosphorus In Tributary Suspended Sediments

The chemical characteristics of the phosphorus carried by the suspended sediments in the tributary samples are listed in Table 2. The various chemically-determined fractions of particulate phosphorus are tabulated therein as percentages of the total particulate phosphorus, the latter of which

TABLE 2. Extractable phosphorus fractions in tributary suspended sediment samples (NaOH-P = sodium hydroxide extractable P, CDB-P = citrate-dithionite-bicarbonate extractable P, HCl-P = hydrochloric acid extractable P, residual-P = total particulate P not extracted with above sequence).

Sample No.	Total Sediment P (μgP/mg dry wgt.)	Extractable fractions (as % of total sediment P) NaOH-P Total	NaOH-P Reactive	CDB-P	HCl-P	Residual P
Maumee River						
5	1.19	26.3	18.5	26.6	9.7	11.0
8	1.20	41.2	23.6	20.3	6.1	12.9
13	1.21	30.0	18.6	18.0	10.4	5.7
17	1.15	26.4	19.7	21.7	10.9	11.4
19	1.07	26.0	20.8	16.0	7.0	12.5
Mean	1.16	30.1	20.3	20.6	8.8	10.6
Sandusky River						
2	1.19	37.9	21.8	—	6.3	13.9
7	1.14	37.0	25.2	18.9	4.8	12.5
11	0.98	37.4	25.4	22.1	5.9	12.6
15	1.10	35.9	22.6	24.7	4.8	2.7
18	0.94	33.8	24.1	15.2	4.6	10.8
22	1.03	22.5	15.0	32.7	5.4	8.6
Mean	1.06	34.2	22.4	22.6	5.4	10.2
Cuyahoga River						
1	1.15	45.0	29.5	—	17.0	9.6
4	1.42	36.1	29.6	22.7	12.4	5.4
12	1.17	50.8	37.8	24.5	17.1	0.5
Mean	1.25	43.4	32.1	23.6	15.3	5.1
Cattaraugus (South Branch)						
6	0.65	17.1	9.1	8.7	37.3	7.6
9	0.52	15.1	9.8	16.9	59.2	10.5
10	0.61	12.4	8.4	11.5	57.1	7.5
20	0.61	6.6	4.3	17.2	49.6	7.2
21	0.61	11.9	7.0	14.5	53.0	7.7
Mean	0.60	12.7	7.7	13.7	50.8	8.0
Genesee River						
3	0.99	24.2	17.2	18.9	27.6	7.8

is given per unit dry weight of sediment. Individual sample data are entered by tributary, and mean values for each variable are given for each tributary to facilitate comparisons among them.

The total phosphorus content of the suspended sediments showed little variation between samples from a given tributary when time-repeat sampling was possible. Instead, fluctuations in total phosphorus levels were more evident among samples taken from different tributaries, and generally higher amounts of sediment phosphorus occurred in samples from the Ohio rivers. The coefficient of variation for total phosphorus in sediments from individual tributaries ranged from a low of 4.9 to a high of 12.0 percent for samples from the Maumee and Cuyahoga Rivers, respectively, while the value computed from the tributary averages was 28.4 percent. Much of the variability between tributaries evident in the latter figure is due to the notably low levels of total phosphorus in the sediments from the Cattaraugus River. Nonetheless, the rivers do show differences in the levels of phosphorus present in their respective suspended sediments.

In the suspended sediments collected from the Maumee, Sandusky, and Cattaraugus Rivers, the total phosphorus content varied by an average of less than 5 percent from the levels found by Logan (1978) in samples taken during the spring - early

summer period of 1977 from the same rivers and at the same sampling locations. The samples obtained by Logan (1978), like those obtained during this investigation, were collected during medium- to high-flow events. These similarities suggest that, during periods of runoff, the phosphorus content of the suspended sediments tends to be a reproducible characteristic for a given tributary.

The single sample of suspended sediments from the Genesee River contained total sediment phosphorus in an amount which was 9.9 percent greater than that found by Reddy (1979, 1980) during a synoptic survey of particulate phosphorus throughout the Genesee basin. The samples analyzed by Reddy (1979, 1980), however, were obtained over a 21-month period and, presumably, at a variety of flow conditions.

The distribution of the chemically-defined fractions of phosphorus in the suspended sediment also showed consistent variations among tributaries and a relative uniformity within samples from a given tributary. Among the tributaries in Ohio, the non-apatite fractions of inorganic phosphorus (reactive NaOH- and CDB-extractable), which have been considered to be of relatively high biological availability (Logan *et al.* 1979b), were the predominant components of particulate phosphorus. Samples from the Cuyahoga River were found to contain the highest amounts of these fractions, while samples from the Maumee and Sandusky Rivers showed lesser, but similar, levels. Acid-extractable inorganic phosphorus contributed least among measured particulate fractions in the two latter tributaries, while in samples from the Cuyahoga, the residual particulate phosphorus was the smallest component. The data given by Logan (1978) showed similar characteristics of particulate phosphorus distribution for these rivers when sampled in 1977.

The particulate phosphorus in samples from the New York rivers, however, was dominated consistently by the acid-extractable (apatite) fraction, which has been suggested to be of low availability (Logan *et al.* 1979b). A comparison of the distribution of phosphorus fractions in the single sample from the Genesee River (Table 2) with the mean values for 17 comparable determinations on suspended sediments from that stream by Reddy (1979), suggests that our sample was atypically low in the HCl-extractable fraction. Other fractions, however, were of similar relative magnitude. Cowen and Lee (1976) noted that particulate phosphorus fractions were quite variable in Genesee River samples taken during the spring of 1973. The phosphorus fractionation data presented by Logan (1978) for suspended matter from the Cattaraugus River showed somewhat higher levels of reductant-soluble particulate phosphorus than those reported here, but the distribution of other fractions showed no differences.

The distribution of particulate phosphorus fractions in the tributaries examined here showed approximately the same degree of variability between samples from different tributaries and among samples from a given tributary as that of the total particulate phosphorus. Accordingly, the tributaries may be classified into two distinct groups with respect to the distribution of phosphorus fractions: the Ohio rivers, which had suspended sediments which were relatively rich in non-apatite forms of phosphorus and low in apatite forms; and, the New York rivers, wherein the sediments were impoverished of non-apatite forms, especially those which were base-extractable, but were enriched in apatite forms of phosphorus. Thus, the distribution of particulate phosphorus forms, like the total phosphorus content, appears to be a relatively constant characteristic for a given tributary during periods of runoff.

Available Phosphorus Bioassays

The results from the bioassays of particulate phosphorus availability may be illustrated conveniently by showing cumulative algal phosphorus uptake as a function of time during the experiment. Shown in Figure 4 are the results of two such bioassays, one for sample 17 (Maumee) and one for sample 18 (Sandusky). The error bars on each data point signify one standard deviation for each triplicate bioassay, while the curves were fit according to the analytical procedure described in the following paragraph.

Since the rate of diffusion of phosphorus across the DCDA membrane and the rate of phosphorus uptake by phosphorus-deficient algae were thought to be at least an order of magnitude larger than typical release rates for available particulate phosphorous (DePinto 1981, Rhee 1973), it was assumed that the rate-limiting step in the conversion of sediment-bound phosphorus to algal phosphorus in the DCDAs was the release of available phosphorus from the sediments. Thus, the rate of accumulation of algal phosphorus should be the same as the rate of release of available phosphorus in the DCDAs. In view of these considerations, the shape of the curves shown in Figure 4

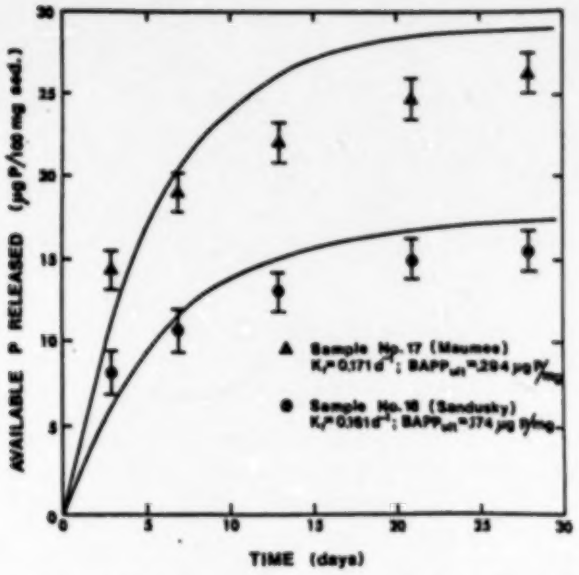

FIG. 4. DCDA bioassay data of cumulative release of available particulate phosphorus from sample nos. 17 (Maumee) and 18 (Sandusky). Solid lines represent fits to equation (1).

strongly suggests that the accumulation of algal phosphorus from sediments, and thus, the release of available phosphorus from the sediments, may be described mathematically by a first order saturation function similar to the BOD equation used in sanitary engineering. In other words, the cumulative available phosphorus release from the particulate matter (BAPP) can be expressed as follows:

$$BAPP(t) = BAPP_{ult} (1-e^{-k_r t}) \qquad (1)$$

where

BAPP(t) = cumulative available P released from suspended sediments in time, t (μgP/100 mg SS)

$BAPP_{ult}$ = ultimate available sediment P release if sediments remained under assay conditions indefinitely (μgP/100 mg SS)

k_r = first-order coefficient for release of available sediment P ($days^{-1}$)

With the aforestated assumptions, the bioassay data on cumulative phosphorus uptake may be substituted for BAPP(t) in Equation 1 and the latter solved directly for the parameters: $BAPP_{ult}$ and k_r.

The results of applying a linear transform of Equation 1 to the bioassay data are given in Table 3

TABLE 3. Rate and extent of phosphorus release from tributary suspended sediments in Dual Culture Diffusion Apparatus experiments.

Sample No.	% of Total Sediment P Released in DCDAs	% of Total Sediment P Ultimately Bioavailable	Release Rate ($days^{-1}$), base e
Maumee River			
5	25.7	31.0	0.182
8	16.0	19.0	0.145
13	13.7	15.6	0.198
14	34.4	37.9	0.080
16	27.3	29.4	0.108
17	22.8	25.6	0.171
19	16.1	18.9	0.192
Mean	22.2	25.3	0.154
Sandusky River			
2	27.0	36.1	0.161
7	13.2	14.2	0.098
11	14.7	16.9	0.200
15	17.8	20.0	0.169
18	16.5	18.5	0.161
22	17.5	18.7	0.146
Mean	17.8	20.7	0.156
Cuyahoga River			
1	29.6	36.1	0.196
4	40.0	47.0	0.216
12	22.3	24.2	0.142
Mean	30.6	35.8	0.185
Cattaraugus (South Branch)			
6	8.3	9.1	0.180
9	0	0	0
10	0	0	0
20	4.0	4.6	0.174
21	13.0	14.9	0.066
Mean	5.0	6.1	0.084
Genesee River			
3	13.5	19.5	0.282

for each sample, by tributary, and mean values for each tributary are given, also. Available particulate phosphorus, as total measured release and as total ultimately available ($BAPP_{ult}$ in Equation 1), is listed as a percentage of the total phosphorus content of each sediment which was analyzed. The release coefficient, k_r, is tabulated as a base e exponent in units of $days^{-1}$.

The availability of phosphorus from sediments from the Maumee River was approximately the same as that found by Dorich, Nelson, and Sommers (1980) for sediments from Black Creek, a

sub-basin within the Maumee watershed. Available sediment phosphorus from Black Creek samples, determined by methods similar to those of Sagher (1976), averaged 20.0 and 21.4 percent of total sediment phosphorus for samples taken in March and June during peak flow conditions. No release rate estimates were given by Dorich *et al.* (1980); however, they noted that the sediment did not release available phosphorus rapidly enough to satisfy uptake by phosphorus-deficient *S. capricornutum*.

Amounts of available phosphorus as a percentage of total phosphorus in suspended sediments collected from the Sandusky River were somewhat less than the amounts found for the Maumee, although values for the individual sample determinations showed a considerable degree of overlapping between the two tributaries. The highest percentage of available particulate phosphorus was found in the Cuyahoga sediment samples, while the lowest quantities of available phosphorus were found in samples from the Cattaraugus River. Verhoff and Heffner (1979) found that particulate matter from a sample of the Cattaraugus collected during a highflow event would not support detectable algal growth at any time during an incubation period of about 160 days. Indeed, two of the Cattaraugus samples tested during this investigation displayed no measureable phosphorus release. The single sample of suspended sediments from the Genesee River contained available phosphorus in amounts which were slightly less than the amounts found in the Sandusky samples, but substantially more than those from samples of the Cattaraugus. Using cell-count methods, Cowen and Lee (1976) estimated that less than 6 percent of total particulate phosphorus in samples from the Genesee River was available to *S. capricornutum*, a considerably lower value than the one found here.

The data on available phosphorus may be cast into a larger context by comparing these results to those obtained in other studies on other types of systems; however, few data are available from other studies involving suspended sediments in rivers. Fluvial sediments from two streams in Ontario were estimated to contain available phosphorus in amounts equal to 24 and 37 percent of the total particulate phosphorus (Williams *et al.* 1980), based on comparing the acid-extractability of algal phosphorus in control cultures of known phosphorus content with that of experimental cultures. Urban runoff, mainly from residential areas of Madison, Wisconsin, contained available particulate phosphorus which averaged 30 percent of the total particulate phosphorus for 13 samples, which were bioassayed using cell-counting techniques (Cowen and Lee 1976). The latter authors additionally determined that up to 23 percent of the particulate phosphorus in snow samples, also from the Madison area, was available to *S. capricornutum*. Young *et al.* (1981) examined the availability of particulate phosphorus in municipal wastewater before, during, and after treatment at four plants in the lower Great Lakes basin and found an average of 63 percent of the total phosphorus in the particulate matter ultimately was available to *Scenedesmus* sp., based on methods similar to those employed in the present investigation. Thus, with the exception of wastewater, the data reported here and the results of PLUARG studies (Sonzogni *et al.* 1980) suggest that the availability of particulate phosphorus in tributary sources to the Great Lakes generally amounts to less than 40 percent of the total quantity.

The available phosphorus release rates for the tributary particulate matter were estimated using Equation 1 and are given in Table 3. The release rates ranged from a high of 0.282 day^{-1} in the single sample from the Genesee River to unquantifiably low values in two samples from the Cattaraugus. The rates of release found for available particulate phosphorus among the Ohio rivers were similar in magnitude and variability from sample to sample. Beyond the generally low values of release rate observed in the Cattaraugus samples, no obvious patterns of occurrence of high and low rates were observed among the tributaries.

The average rate of release for all samples in this investigation was 0.154 day^{-1}. This value, though not directly comparable, greatly exceeds the value of 0.087 percent per day reported by Verhoff and Heffner (1979), based on the overall conversion of total particulate phosphorus to algal phosphorus for samples from the Sandusky River.

DISCUSSION

Kinetics of Sediment Phosphorus Availability

As sediment-bound phosphorus enters the lakewater environment from a tributary source, it can undergo various physical-chemical and biological reactions including: sorption-desorption; dissolution-precipitation; microbial mineralization of organic phosphorus; microbial utilization or

microbial-induced dissolution of particulate phosphorus; and coagulation-sedimentation of the sediment material. The factors that will affect the algal availability of the particulate phosphorus while it is in the water column are the same ones that govern the above reactions: temperature; soluble reactive phosphorus in the lake water; lake morphometry, hydrology, and mixing dynamics; size, density, and physiochemical characteristics of the particles; phosphorus fractionation (form of phosphorus compounds) of the particles; and lake productivity level, including microbial activity and degree of phosphorus limitation. Therefore, the amount of particulate phosphorus made available for algal uptake while the river sediment is in the water column depends not only on the extent and direction of the above reactions but on the respective rates.

The western basin of Lake Erie, for example, has a mean hydraulic retention time of about 1.5 months (Rumer 1978), although this is certainly shorter during storm events. Furthermore, our initial measurements on Maumee River samples suggest a median particle diameter on a volume basis of about 3 μm for sediment particles entering the western basin during high flow events. Assuming a sediment density of 2.5 gm/cm^3 and a mean depth of 7.3 m for the western basin, Stoke's law would predict that 50 percent of the particle volume (and, therefore, half of the mass, assuming a constant density) would settle into the bottom sediments in about 10 days. Although these estimates are admittedly crude, comparison with available phosphorus release rates measured in this study (Table 3) indicates a strong probability that river suspended sediment material will settle to the lake bottom or be transported a considerable distance before all the potentially available phosphorus has been released. It would, therefore, seem essential that dynamic water quality models properly account for the rate at which allochthonous particulate phosphorus is made available in the water column of a lake.

Most deterministic nutrient-phytoplankton models currently being applied to the Great Lakes do, in fact, have a mechanism for converting allochthonous "unavailable" phosphorus (generally defined as total tributary phosphorus minus soluble reactive phosphorus) to available phosphorus (Bierman *et al.* 1980, DiToro and Matystik 1980, DiToro and Connolly 1980, Rodgers and Salisbury 1981). However, there are subtle differences between the approach used by these models and our observations in the DCDAs. As illustrated in Figure 4, our data suggest that the rate of release of available phosphorus from suspended sediments is a first-order function of the amount of potentially available phosphorus remaining on the sediments. On the other hand, current models treat the rate of release as a first-order function of the remaining total particulate ("unavailable") phosphorus, although their rate coefficients are generally lower than those measured in this study. In other words, the current models make no distinction between the rate of conversion of allochthonous "unavailable" phosphorus (primarily inorganic sediment phosphorus) and the rate of conversion of autochthonous "unavailable" phosphorus (primarily algal-bound phosphorus).

Illustrated in Figure 5 and superimposed on our DCDA data are the two methods for predicting the cumulative available phosphorus released from sample 17 sediments (Maumee River). Our method would predict the available phosphorus released versus time according to the following equation:

$$BAPP(t) = 29.4\,[1 - \exp(-0.171t)] \qquad (2)$$

where

BAPP(t) = cumulative available phosphorus released from sediments (μgP/100 mg dry sediment)
29.4 = ultimate available phosphorus on Maumee River sample 17 sediments (μgP/100 mg dry sediment)
0.171 = rate of release of available phosphorus from sediments (days^{-1})
t = incubation time of sediments in the lake water column (days)

Assuming a temperature of 20°C in a highly productive system like Lake Erie, DiToro and Connolly (1980) would predict available phosphorus release from this sediment according to

$$BAPP(t) = 115\,[1 - \exp(-0.03t)] \qquad (3)$$

where

115 = total particulate phosphorus on Maumee River sample 17 sediments (μgP/100 mg dry sediment)
0.03 = rate of conversion of "unavailable" phosphorus to available phosphorus at 20°C (days^{-1})

These two predictions are reasonably similar for the first 7 or 8 days; thereafter, however, the

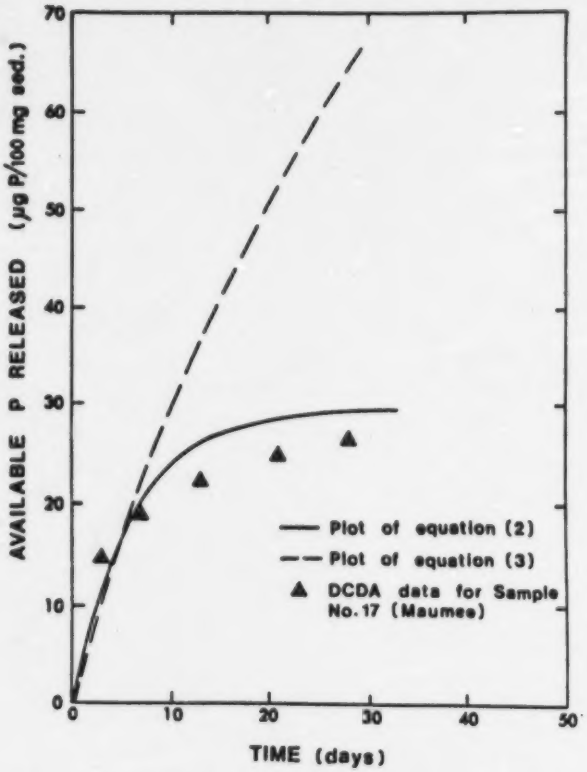

FIG. 5. Comparison of current Great Lakes model predictions of BAPP versus time (equation (3)) with actual data for sample no. 17 and first-order fit (equation (2)).

modeling prediction considerably overpredicts the observed data. Virtually all of our samples behaved in a similar fashion to sample 17 when tested against the two prediction methods; some demonstrated even more deviation, depending on the relative amount of ultimately available particulate phosphorus to total particulate phosphorus.

The implications of the above analysis are quite obvious. For systems in which the tributary sediment particles do not reside long in the water column (less than about 10 days), either Equation (2) or (3) would yield reasonable results. On the other hand, when tributary sediments reside in the water column longer than about 10 days, there would be a tendency for models calibrated primarily on algal biomass to predict an unrealistic buildup of soluble phosphorus in the lake. In turn, this might lead to either an overestimate of the phosphorus retention time or an unrealistic adjustment of other model coefficients in order to effect a calibration. It also might lead to an exaggeration of the importance of certain phosphorus sources in affecting biological production.

One final observation on the kinetics of sediment phosphorus availability is also illustrated in Figure 4. In many of our samples, our first-order fits tended to underpredict the observed DCDA at the start of a run and overpredict the data at the end of a run. Also, the observed phosphorus release did not seem to be leveling off as rapidly as the prediction. This observation, in combintion with the statistical analysis of the NaOH-P and CDB-P fractions considered below, suggests that there are, perhaps, two first-order release mechanisms being observed: (1) a relatively rapid release based on the NaOH-P fraction of the sediment phosphorus, and (2) a much slower and consequently longer-lasting release of the CDB-P fraction. The superposition of these two first-order mechanisms might better fit the observed data; however, more samples and experimentation are necessary to confirm this postulate.

Sediment Phosphorus Characteristics and Bioavailability

Relationships between biologically available phosphorus in the suspended solids of the tributary samples and the various chemically-defined fractions were examined initially by computing simple product-moment correlation coefficients between the chemical fractions and bioavailability characteristics. The results of these calculations, based on data from all tributary samples, are presented in Table 4. The data in Table 4 show the existence of a close relationship between amounts of available phosphorus and either total phosphorus or nonapatite inorganic fractions (reactive NaOH-P and CDB-P) of phosphorus associated with tributary suspended matter. The available phosphorus release rate, however, was poorly correlated with the phosphorus forms which were measured.

Available particulate phosphorus, measured directly by bioassay (short-term available) or calculated by first-order analysis of the bioassay data (ultimately available), was most closely correlated with the total phosphorus content of the particulate matter. Such a relationship, however, has a limited application beyond the data reported here. This is true since the total phosphorus in suspended sediments from natural systems characteristically is not a single, uniform substance. Rather, it consists of several components which vary in their proportions and in their relative availabilities. In particular, the

TABLE 4. Simple correlation coefficients (r) between bioavailability parameters and chemically extracted fractions of particulate phosphorus in lower lakes tributary samples. $N = 20$, $r > 0.444$ at $\alpha < 0.05$ for testing H_o: $\rho = 0$.

Particulate Phosphorus Fraction	Available Phosphorus		
	Short-Term	Ultimate	Release Rate
Total P	0.857	0.848	0.575
Total NaOH-P	0.770	0.754	0.412
Reactive NaOH-P	0.819	0.793	0.429
CDB-P	0.804	0.782	0.459
HCl-P	-0.415	-0.392	-0.376
Residual P	0.328	0.362	0.228

components of the total sediment phosphorus with significant relationships to biological availability were found to be associated mainly with the reactive NaOH-, and CDB-extractable fractions.

The reactive NaOH-extractable phosphorus was the predominant component of the total NaOH-extractable fraction (68 percent) and gave the strongest correlation with available phosphorus of all the particulate phosphorus fractions. Although the non-reactive NaOH-extractable fraction, which consists of base-extractable particulate organic phosphorus and, possibly, condensed phosphates, was related to the reactive NaOH-extractable fraction ($r = 0.744$), it correlated only marginally with either the short-term or ultimately available particulate phosphorus ($r \sim 0.53$ with both available fractions). The latter correlations, although significant statistically ($\alpha < 0.05$), are spurious and result from the tendency for both reactive and nonreactive NaOH-extractable particulate phosphorus to occur in constant proportions in our samples rather than to significant biological availability of the non-reactive fraction. Thus, these data support the conclusion that the inorganic fraction of base-extractable particulate phosphorus has a relatively high biological availability, as suggested by others (Williams *et al.* 1980, Sagher 1976, Cowen and Lee 1976) who have examined the availability of phosphorus associated with particulate matter from a variety of sources.

The reductant-soluble (CDB-extractable) fraction of particulate phosphorus in the tributary samples also correlated well with the short-term and ultimately-available particulate phosphorus. To an extent, however, intercorrelation between amounts of reactive NaOH- and CDB-extractable phosphorus ($r = 0.774$) in the sediment samples magnified the apparent relationship between reductant-soluble and available particulate phosphorus. Consequently, the intercorrelation also confounds the relationship between reactive NaOH-extractable and available phosphorus. It is possible, nonetheless, to examine independently the association between available phosphorus and either of the two correlated, chemically-defined phosphorus fractions by mathematically partialling out the effects of either interfering fraction (Thorndike 1978). This was done for the two fractions under discussion and the results are given in Table 5. As suggested by the partial correlation data in Table 5, both of the non-apatite inorganic phosphorus fractions showed significant correlation with the available phosphorus measured directly during the bioassay; however, the reactive NaOH- and CDB-extractable phosphorus ($r = 0.774$) in the sediment samples magnified the apparent relationship between reductant-soluble and available particulate phosphorus. Consequently, the intercorrelation also confounds the relationship between reactive NaOH-extractable and available phosphorus. It is possible, nonetheless, to examine independently the association between available phosphorus and either of the two correlated, chemically-defined phosphorus fractions by mathematically partialling out the effects of either interfering fraction (Thorndike 1978). This was done for the two fractions under discussion and the results are given in Table 5. As suggested by the partial correlation data in Table 5, both of the non-apatite inorganic phosphorus fractions showed significant correlation with the available phosphorus measured directly during the bioassay; however, the reactive NaOH-extractable fraction showed better correlation with the ultimately available particulate phosphorus than did the CDB-extractable fraction. The latter result was unexpected inasmuch as the CDB-extractable fraction is often considered to be available over long rather than short periods of time

TABLE 5. First-order partial correlation coefficients between biologically available phosphorus and non-apatite inorganic phosphorus fractions in suspended particulate matter from lower lakes tributaries. $N = 20$, $r > 0.456$ at $\alpha \leq 0.05$.

Phosphorus Fraction	Available Phosphorus	
	Short-Term	Ultimate
Reactive NaOH-P	0.522	0.462
CDB-P	0.468	0.455

(Logan 1978). One would anticipate, therefore, that the CDB-extractable fraction would correlate more closely with the ultimately available phosphorus than with the short-term available fraction, but this was not observed.

It is possible, however, that the methods used here for estimation of ultimately available phosphorus in suspended matter were biased against determining the special importance to availability of the reductant-soluble phosphorus fraction over a long time period. Such a bias would result if available particulate phosphorus were released from the CDB-extractable fraction at a slower rate than from the reactive NaOH-extractable fraction. If this were the case, then the ultimately available phosphorus could be underestimated by the method reported here, depending on the relative difference in release rates, since it was calculated on the assumpiton that a single, first-order rate governed the process of available phosphorus release under the conditions of the bioassay. Further experimental work could clarify this question. Nonetheless, it is apparent from the data collected in this investigation that both the reactive NaOH- and the CDB-extractable fractions of particulate phosphorus independently released phosphorus which was biologically available to algae.

As noted earlier, the available phosphorus release rate coefficients correlated poorly with the chemically-defined fractions of particulate phosphorus in the samples (Table 3). Total particulate phosphorus and the CDB-extractable fraction were the only measured quantities which were determined to have a relationship to the rate of release. The correlation between release rate and the reductant-soluble fraction was spurious, however, and resulted from the dependency of the CDB-extractable fraction on the level of total particulate phosphorus ($r = 0.879$). This means that, for our samples, available phosphorus was released at a rate which depended directly on the amount of phosphorus per unit weight of solid matter, regardless of chemical form. This dependency, however, was biased strongly by the samples obtained from the Cattaraugus River. The release rate for available phosphorus from the Cattaraugus samples, as seen from the data in Table 3, generally was low compared to the rates found for samples from other tributaries. The total phosphorus content of the sediments from the Cattaraugus also was considerably less than that found in the other tributaries (Table 2). Furthermore, exclusion of the Cattaraugus samples from the data reduces the correlation between the available phosphorus release rate and total phosphorus to an insignificant value. Thus, factors which were unquantified during this investigation appear to control the rate of release of available phosphorus from particulate matter in the tributary samples, while the state of the particulate phosphorus, as determined by chemical fractionation, shows no clear rate-controlling influence. It would seem, however, that such sediment characteristics as particle size distribution, phosphorus fractionation by particle-size class, and microfloral density could affect the rate of available phosphorus release and, thus, might be considered in future investigations of the release of available phosphorus from particulate matter.

SUMMARY AND CONCLUSIONS

Samples of suspended sediment from five tributaries to the lower Great Lakes were collected during runoff events in the period March-June, 1980. The phosphorus content of the particles was fractioned into several chemically-defined forms, and a direct assessment of the biological availability was performed using a first-order model to describe the release of available phosphorus from the sediments. From these data the following conclusions were drawn:

1. Total sediment-bound and available particulate phosphorus consistently was greater in Ohio tributaries (Maumee, Sandusky, and Cuyahoga Rivers) than those in New York (Cattaraugus and Genesee Rivers).
2. Suspended sediments from Ohio tributaries were relatively rich in non-apatite but poor in apatite forms of phosphorus in comparison with those collected from the New York streams.
3. Available particulate phosphorus showed a direct dependence on both the reactive NaOH- and CDB-extractable fractions of particulate phosphorus and generally amounted to less than 40 percent of the total particulate phosphorus in the tributary samples.
4. The rate of available phosphorus release from the tributary sediments was generally independent of the observed sediment characteristics.
5. A first-order model of available phosphorus release from aquatic particulate matter, based on a rapid release from an ultimately available fraction of total particulate phosphorus, appeared to more realistically describe in-lake phosphorus dynamics than current models based on a low-rate of conversion of total particulate phosphorus.

Determination of the relative availabilities of the two non-apatite fractions of particulate inorganic phosphorus and identification of factors which control the release rate of available particulate phosphorus were identified as areas which require further research.

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